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DTU Fotonik
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Morphology of Copper Tin Sulfide Films Grown by Pulsed Laser Deposition at 248 and 355 nm

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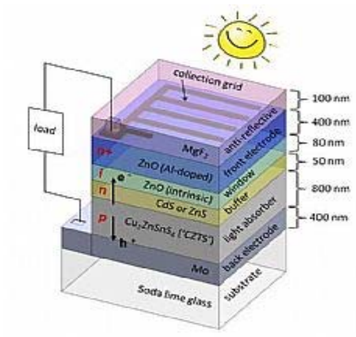
Thin films solar cells based on Cu_2ZnSnS_4 (CZTS) as absorber layer have seen a rapid development leading to a world record of 8.8% [1].

However, other p-type semiconductors with fewer elements and reduced complexity compared to CZTS are also available, such as ternary Cu–Sn–S systems, i.e. Cu_2SnS_3 (CTS) [2].

Properties of CTS as absorber layer in solar cell

- ❑ Band gap of ~ 1.0 eV (CZTS 1.45 eV) and absorption coefficient comparable to CZTS (~10^4 cm $^{-1}$) [3].
- ❑ It consists of environmentally friendly and abundant elements.
- ❑ Reduced complexity compared to CZTS.



Choice of PLD

- ➢ The CTS absorber layer has a complex stoichiometry
- ➢ Its composition needs be accurately controlled

Sn and S losses are commonly observed in CTS films, thus a SnS-enriched CTS system is also studied here.

Motivation and aim

First CTS solar cell prepared by Pulsed Laser Deposition have reached an efficiency of 0.82%. [4]

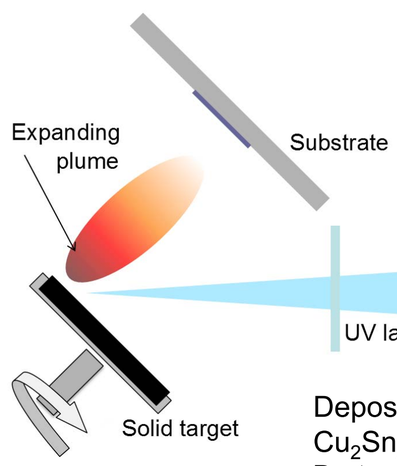
To best of our knowledge, we were the first group to report on CTS thin films by Pulsed Laser Deposition (PLD) [5].

Ablation of CTS at 355 nm results in large droplets and rough surfaces and the aim of the study is to reduce their size and distribution.

Here we study the influence of the laser wavelength on the size and density of the droplets using:

1. Two different wavelengths, i.e. **355 nm (Nd:YAG laser, third harmonic**) and **248 nm (KrF excimer laser**).
2. Two different targets, i.e. **CTS** and **SnS enriched-CTS** to compensate for losses of Sn and S in the CTS films

The Pulsed Laser Deposition Route

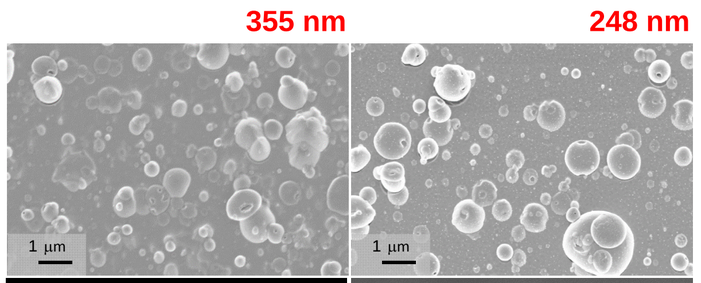


	λ = 355 nm	λ = 248 nm
	Nd:YAG	KrF excimer
	τ = 5-7 ns, ν = 10Hz	τ ~ 20 ns, ν = 10Hz
	A= 2.1-2.5 mm²	A = 2.2 mm²
	F= 0.4-2.3 J/cm²	F = 0.4-2.2 J/cm²
	D = 4-4.5 cm (target-substrate dist.)	D = 4 cm

Deposition of Cu_2SnS_3 and SnS-enriched Cu_2SnS_3, i.e. $Cu_2Sn_2S_5$

Post annealing in sulfur atmopshere at 570 C using sulfur powder in a N_2 gas

Surface morphology



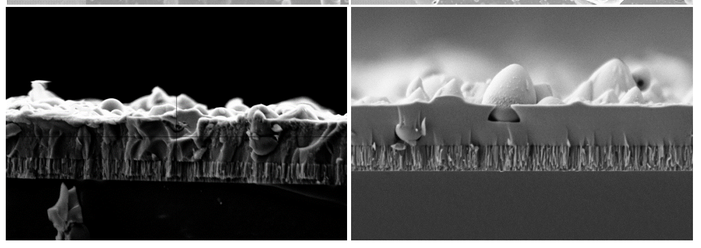


Figure 2. SEM images (top and side view) of **as-deposited Cu_2SnS_3** films on Mo-coated soda-lime glass

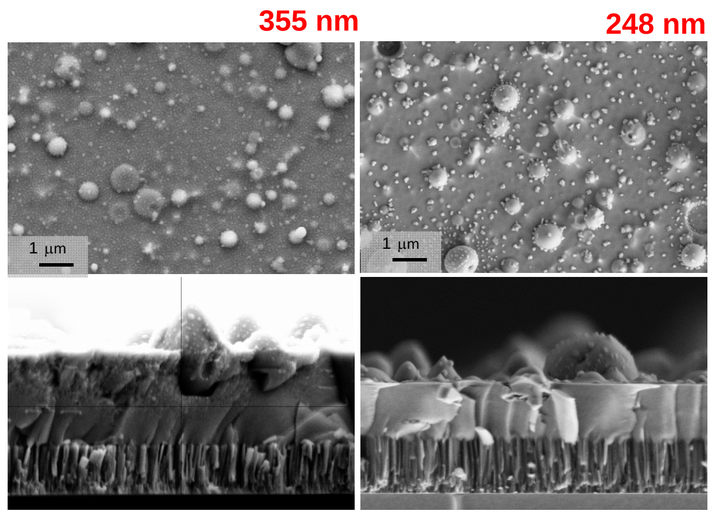
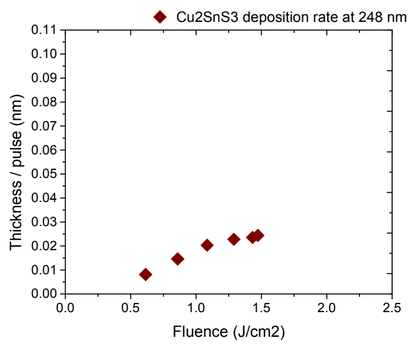
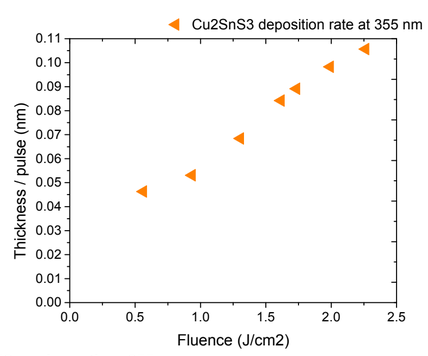


Figure 3. SEM images (top and side view) of **as-deposited SnS-enriched Cu_2SnS_3** films on Mo-coated soda-lime glass

Deposition rate measurements

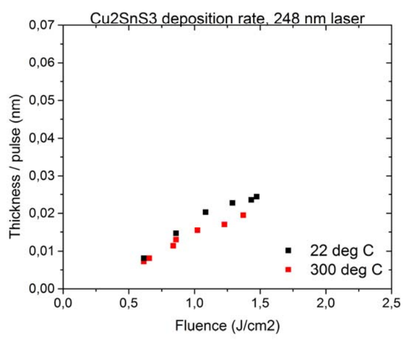
Wavelength dependence on the deposition rate

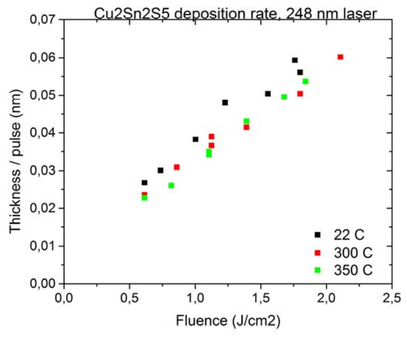




Lower deposition rate for Cu2SnS3 at 248 nm laser than 355 nm

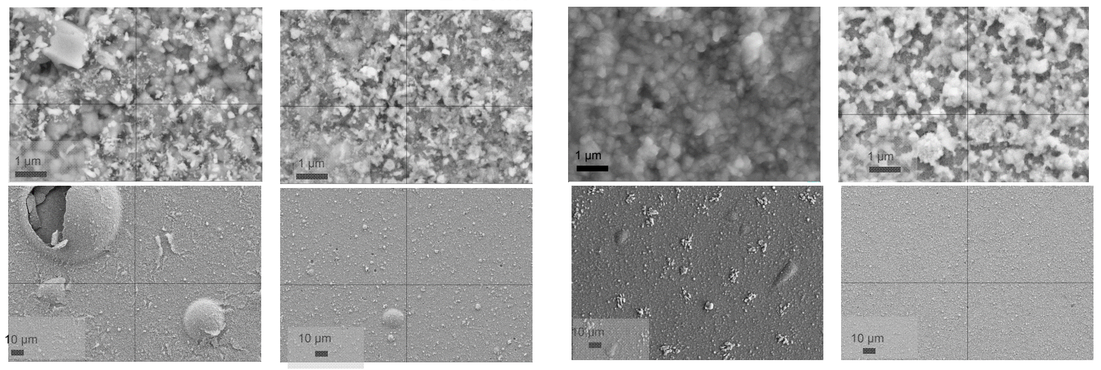
Composition dependence of the deposition rate





Higher deposition rate for SnS-enriched Cu2SnS3 than Cu_2SnS_3

Annealing of CTS and SnS enriched-CTS



Discussion and conclusion

- SEM images reveal that CTS and SnS-enriched CTS absorber layers have droplets ranging from hundreds of nanometers up to several micrometers.
- A lower irradiation wavelength (higher photon energy) does not reduce the density or size of the droplets.
- Droplets are generally Sn and S-poor suggesting losses of volatile elements during re-crystallization of the molten agglomerates arising from the ablation process.

- Annealing reduces considerably the size and distribution of droplets; however, local non-uniformity composition may be retained in the annealed films.
- Bubbles are present on the surface of the annealed films, most probably resulting from evaporation of SnS.

- Further studies will be carried out to understand the influence of droplets on the performance of the solar cells but also to reduce their density by optimization of the PLD process

Acknowledgement

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